John von Neumann Institute for Computing

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published in

NIC Symposium 2001, Proceedings,
Horst Rollnik, Dietrich Wolf (Editor),
John von Neumann Institute for Computing, Jülich,
NIC Series, Vol. **9**, ISBN 3-00-009055-X, pp. 61-62, 2002.

http://www.fz-juelich.de/nic-series/volume9

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Computational Chemistry, which was started by a handful of quantum chemists in the 1950s and 1960s, has achieved in the last decade its firm position among the other disciplines of chemistry, in molecular physics and pharmacy. In some areas, such as the determination of molecular structures or relative stabilities of molecules, it has become a complementary tool to experimental investigations. In many other areas, however, in which details of the microscopic behaviour must be known in order to understand the mechanisms and course of a chemical reaction, computational chemistry may be the only tool to study binding interactions or properties of short-lived intermediates. These investigations should be performed in close connection with measurements which in general observe only starting material and final products depending on the experimental situation. There are even some questions which can only be answered by computations, for example if molecules cannot be synthesized or have very short life times under given conditions; typical such study areas are reactions in the atmosphere or in interstellar space. Many of such investigations are undertaken on powerful workstations. For large molecules, however, in particular approaching the biological regime, and for very complex molecules, whose investigation requires unusual high accuracy, high-performance computers such as available at the NIC are required.

The following articles represent typical examples for to-days chemical investigations. The computational methods employed range from simple force-field molecular mechanics (MM) methods to more or less routine quantum chemical (QC) procedures such as density functional theory (DFT) and self-consistent-field (SCF) calculations with additional Møller-Plesset (MP2) perturbation corrections, all the way to high-level QM methods such as coupled cluster (CCSD(T)) procedures or multi-reference configuration interaction (MR-CI) procedures. For large systems combined treatments are in use, combining quantum mechanics for the description of subtle details with molecular mechanics (QM/MM) for the less important part of the systems. Simulation methods such as molecular dynamics (MD) are also essential and have been improved for certain applications.

The various contributions show very clearly the great importance of the close cooperation between the experimentalist and the computational chemist. Most of the results would not have been obtained if each of the researchers had stayed within his own discipline.

Binding properties in protein nucleic acids, in particular hydrogen (pairing) bonds and van der Waals (stacking) properties are studied by modifying the backbone of a DNA strand in order to be able to better differentiate between these types of interactions. The synthesis of the modified duplex, in which the complicated geometrical conditions of the helical double strand DNA are strongly simplified, was essential in this regard. The role of transition metal centers in catalytic and enzymatic active sites is studied in two contributions. The biological catalytic activity of vanadium-containing enzymes could be characterized by chemical, biochemical and crystallographical data, but only computations are in a posi-

tion to get more information on the molecular mechanism of the reactions at the active site and on possible reaction intermediates. Organometallic molecular catalysts have unprecedented selectivity, and their efficiency can be compared with the astounding selectivity of enzymes. Hence it is an obvious goal to design such catalysts - in this case based on an chiral rhodium compound. An obvious problem, as in many such calculations, is the lack of force field parameters involving transition metals bonding. The parallel computing environment at the NIC was essential to use the newly developed Genetic Algorithm for the extensive geometrical and force constant optimization. A further contribution shows how experimental results on the study of liquid surfaces can be supplemented by simulation. Electron spectroscopy is able to give information on vertical diffusion within a small surface layer, while MD simulations can be used as ideal tool to study lateral movement and to gain details of inner surfaces. In this combination the ordering processes at the interface liquid/vacuum and the traffic between the bulk and the surface could be established. The last two contributions deal with theoretical developments of quantumchemical methods. The first develops multi-reference configuration interaction procedures, based on determinantal basis functions, and makes use of 128 nodes of parallel computing. Almost perfect scaling between 48 and 128 nodes is achieved. This new development allows to treat CI expansions up to 5x109 terms of which up to 5x106 are included in the variational wavefunction. The code allows to treat medium-sized molecules with up to 100 electrons with very high accuracy, in ground and electronically excited states. This code is a major step forward to treat electron correlation in a proper way which allows to compute with high accuracy entire potential energy surfaces. The second theoretical advance shows how to calculate rovibronic energy levels for tetraatomic molecules. Such development would also not have been possible on a computer of work-station size. A straightforward treatment of such a problem would require several million basis functions to achieve a good description of the vibrational motion, a six-dimensional potential energy surface and the diagonalization of the hamiltonian matrix of the same order as the number of basis functions. Clever computational stepwise strategies led to a general code with impressive performance. It will be very valuable to guide spectroscopic assignments.

All examples demonstrate the power of computational chemistry and the essential role of the John von Neumann Institute for Computing.